Crystal Structure of a Binuclear Copper(II) Complex with μ-Alkoxo and μ-Pyridonato Bridges. Effect of the Dihedral Angle on the Superexchange Interaction

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Binuclear Copper(II) Complex, Superexchange Interaction, μ-Pyridonate Bridge

The crystal structure of the binuclear copper(II) complex, $[Cu_2(L)(2\text{-pyridonato})]$ was determined by X-ray diffraction, where $H_3(L)$ represents the Schiff base ligand derived from 1,3-diaminopropane-2-ol and acetylacetone. Two copper(II) ions are bridged by alkoxide and 2-pyridonate groups with a Cu–Cu separation of 3.249(2) Å. Ferromagnetic interaction is found to be operating in this complex, which is attributed to the small dihedral angle (121°) between the two planes containing the copper(II) ion.

1. Introduction

The studies on magnetic polynuclear complexes started in 1952, when Bleaney and Bowers demonstrated that the magnetic and ESR properties of copper(II) acetate were due to the dimeric nature of the molecule [1]. These authors established a theoretical expression for the magnetic susceptibility of such a system as a function of the temperature and the energy parameter J characterizing the interaction between the Cu(II) ions in the same molecule entity. Many researchers then attempted to rationalize the sign and the value of J in terms of the structural data. The most elegant correlation between structural and magnetic properties was established by Hatfield and Hodgson, who showed that the magnitude of the interaction in planar dihydroxo-bridged copper(II) dimeric complexes depends on the Cu–O–Cu bridging angle [2, 3].

In 1975, Hoffmann *et al.* [4] have given the first reliable theoretical calculation on J values on the basis of the simple "extended Hückel MO", and succeeded in explaining the correlation observed by Hatfield and Hodgson. After this, de Loth *et al.* [5] reported an *ab initio* calculation on J of copper(II) acetate and pointed out that the superexchange mechanism considered by Hoffmann *et al.* is only a part of the many contributions. In 1985, Nishida *et al.* [6] have observed the appearance of the "orbital countercomplementary effect" in some binuclear copper(II) complexes and confirmed that Hoffmann's treatment based on the simple "extended Hückel MO" is more appropriate to visualize the superexchange interaction.

In this study we have prepared and determined the crystal structure of a new binuclear copper(II) complex bridged by alkoxide and 2-pyridonate anion in order to contribute to the knowledge on this problem.

2. Materials and Methods

Synthesis

The Schiff base ligand $H_3(L)$, derived from 1,3-diaminopropane-2-ol and acetylacetone, was prepared according to the published method [6].

$Cu_2(L)Cl \cdot H_2O \cdot CH_3OH$

From the methanol solution of $CuCl_2 \cdot 2H_2O$ (0.002 mol), H_3L (0.001 mol), and triethylamine (0.003 mol), a green precipitate was obtained.

$Cu_2(L)Cl \cdot H_2O \cdot CH_3OH$

Calcd	C 36.20	H 5.17	N 6.25	Cu 28.38,
Found	C 36.20	H 5.09	N 6.08	Cu 28.6.

$[Cu_2(L)(2\text{-pyridonate})]$

From the reaction mixture (methanol solution) of $Cu_2(L)Cl \cdot H_2O \cdot CH_3OH$ (0.001 mol), 2-pyridone (0.001 mol) and triethylamine (0.001 mol), the desired complex was obtained as dark green needles and recrystallized once from a dmf-methanol solution.

$[Cu_2(L)(2\text{-pyridonate})]$

Calcd	C 45.76	H 4.91	N 8.87,
Found	C 45.71	H 4.89	N 8.90.

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Table I. Crystal data of [Cu_2(L)(2-pyridonate)].

Formula	$Cu_2O_4N_3C_{18}H_{24}$
Molecular weight	473.5
Space group	$P2_1/n$
a [Å]	23.808(7)
b [Å]	8.353(2)
c [Å]	9.548(4)
β [°]	92.57(3)
V [$Å^3$]	1897
Z	4
d_c/g cm^{-3}	1.66
μ(MoKα) [cm^{-1}]	23.5
F(000)	996
Reflections observed	3752
Reflections > $3\sigma\|F_o\|$	2717
R (= $\Sigma\|\|F_o\|-\|F_c\|\|/\Sigma\|F_o\|$)	0.072
R_2 (= $(\Sigma\|\|F_o\|-\|F_c\|\|^2/\Sigma\|F_o\|^2)^{1/2}$)	0.099
Largest peak [e$Å^{-3}$]^a	0.67
Number of parameters	245

^{a} Largest peak in the final difference-Fourier map.

X-ray data collection

The crystal was mounted on a Rigaku AFC-5 four-circle automatic diffractometer with graphite monochromated MoKα radiation (λ = 0.71069 Å). Automatic centering and the least-squares routines were carried out on 25 reflections to obtain the cell constant given in Table I. The $\theta-2\theta$ scan technique was employed to record the intensities of a unique set of reflections with $3° < 2\theta < 55°$. Three check reflections were measured every 100 reflections; they exhibited no significant decay during the data collection. Intensities were corrected for Lorentz and polarization effects.

Structure solution and refinement

The positional parameters of the two copper atoms were determined by direct methods [7]. The remaining non-hydrogen atoms were located in subsequent Fourier maps. The refinement was done by using anisotropic thermal parameters. In the last stage of refinement, the difference Fourier map showed no significant peaks and all the parameters shifts were less than 0.4σ. Programs used for the structure solution and anisotropic refinement were supplied by the local version of the UNICS system [8]. Atomic scattering factors were taken from the International Tables [9]*.

Magnetic measurements

Magnetic susceptibility (χ) was measured by Dr. T. Tokii at Saga University using the Faraday method in the temperature range 81.1−297.7 K. Magnetic moments were calculated by the equation $\mu_{eff} = 2.878\sqrt{\chi T}$.

3. Results and Discussion

The complex [Cu_2(L)(2-pyridonate)] crystallizes in the monoclinic space group $P2_1/n$. The final atomic parameters are listed in Table II and important bond distances and angles are summarized in Table III. As shown in Fig. 1, two copper(II) ions are bridged by alkoxide and 2-pyridonate anions. The copper-ligand bond distances are in the range of Cu−N and Cu−O distances observed for similar complexes [6, 10, 11]. The geometries around both the copper(II) ions are best described as square planar. It should be noted here that the dihedral angle between the two planes, (Cu1, O1, O3, N1, and N3) and (Cu2, O2, N2,

Table II. Atomic coordinates ($\times 10^4$) of [Cu_2(L)(2-pyridonate)] with estimated standard deviations in parenthesis. Thermal parameters are given by equivalent temperature factor (B_e).

Atom	x	y	z	B_e
Cu1	1632(1)	4013(2)	2122(1)	2.22(3)
Cu2	2979(1)	4199(2)	1726(1)	2.14(3)
N1	1682(4)	5044(11)	3941(9)	2.58(22)
O1	854(4)	4502(11)	1807(8)	3.83(23)
O3	2369(3)	3113(9)	2623(7)	2.42(18)
N2	3416(4)	3806(11)	3450(9)	2.67(22)
O2	3570(3)	5335(11)	878(8)	3.54(22)
C1	− 83(6)	5285(23)	2204(15)	5.59(49)
C2	534(5)	5200(16)	2672(13)	3.78(34)
C3	716(5)	5865(15)	3965(13)	3.45(31)
C4	1273(5)	5771(14)	4563(12)	3.06(29)
C5	1382(6)	6570(17)	6006(13)	4.12(36)
C6	2250(5)	4883(13)	4604(11)	2.67(27)
C7	2460(5)	3204(13)	4145(10)	2.42(25)
C8	3086(5)	2948(14)	4510(11)	2.88(28)
C9	3963(5)	4012(15)	3632(12)	3.02(28)
C10	4268(6)	3285(18)	4931(13)	4.16(36)
C11	4286(5)	4856(15)	2667(12)	3.22(30)
C12	4079(5)	5517(14)	1408(13)	3.05(29)
C13	4466(5)	6485(17)	506(14)	3.85(34)
O4	2564(3)	4331(10)	− 65(8)	3.06(20)
C25	2147(5)	3497(12)	− 589(10)	2.31(24)
C24	2177(5)	2865(15)	−1971(11)	3.18(30)
C21	1231(5)	2422(15)	− 453(12)	3.36(31)
N3	1676(4)	3272(11)	135(9)	2.53(22)
C23	1723(6)	1983(15)	−2527(12)	3.50(32)
C22	1245(6)	1784(16)	−1772(12)	3.69(33)

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* Complete tables of atomic coordinates and anisotropic thermal parameters and observed and calculated structural factor amplitudes have been deposited at the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2. The Registry-Nr. CSD 53633, the name of the author, and the reference should be given.

Table III. Selected bond lengths [Å] and angles (°) of the coordination sphere in $[Cu_2(L)(2\text{-pyridonate})]$.

Cu1–Cu2	3.249(2)	Cu1–N1	1.937(9)
Cu1–O1	1.908(9)	Cu1–O3	1.948(7)
Cu1–N3	2.002(9)	Cu2–O3	1.944(7)
Cu2–N2	1.935(9)	Cu2–O2	1.908(8)
Cu2–O4	1.939(7)		
Cu1–O3–Cu2	113.2(4)	O3–Cu1–N3	91.7(3)
O3–Cu1–O1	168.1(4)	O3–Cu1–N1	86.2(3)
N1–Cu1–O1	93.8(4)	N1–Cu1–N3	169.4(4)
O1–Cu1–N3	90.4(4)	O3–Cu2–N2	85.9(3)
O3–Cu2–O2	177.9(3)	O3–Cu2–O4	93.1(3)
N2–Cu2–O2	93.8(4)	N2–Cu2–O4	173.1(4)
O2–Cu2–O4	87.4(3)		

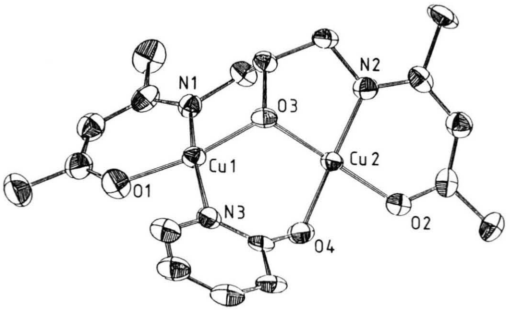


Fig. 1. ORTEP drawing of $[Cu_2(L)(2\text{-pyridonate})]$.

O3, and O4), is 121°, deviating remarkably from 180°.

The temperature dependence of the magnetic susceptibility is shown in Fig. 2. The magnetic moments are 1.91 and 2.05 μ_B at 297.9 and 81.1 K, respectively. The $2J$-value based on the Bleaney-Bowers equation is $+62.8\ \text{cm}^{-1}$, indicating that weak ferromagnetic interaction is operating in this complex. This behaviour is quite different from that of the analogous derivatives, such as $[Cu_2(L)(CH_3COO)]$ and $[Cu_2(L)(C_6H_5COO)]$, where weak antiferromagnetic interaction is operating [6].

In planar copper(II) complexes an unpaired electron resides in a d_{xy} orbital, and the symmetric and antisymmetric combinations of these orbitals are expressed as in equations (1) and (2) (for the definition of x and y coordinates, *cf.* Fig. 3). According to Hoffmann *et al.* [4] and Kahn *et al.* [12],

$$\varphi_a = d_{xy} + d'_{xy} \qquad (1)$$

$$\varphi_s = d_{xy} - d'_{xy} \qquad (2)$$

the $-2J$ value in the binuclear copper(II) complexes can be expressed as shown in equation (3),

$$-2J = J_{AF} - J_F \qquad (3)$$

where J_F and J_{AF} represent the ferromagnetic and antiferromagnetic contributions, respectively, both

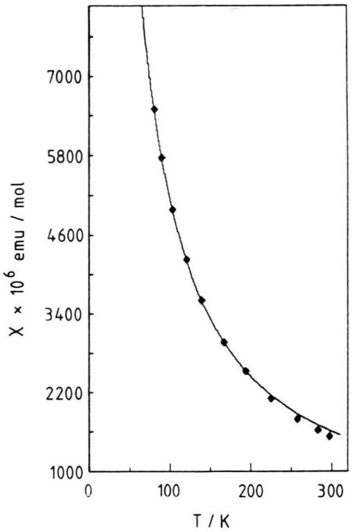


Fig. 2. Temperature dependence of magnetic susceptibility of $[Cu_2(L)(2\text{-pyridonate})]$. ◆◆◆ observed value; ——— calculated value based on the Bleaney-Bowers equation where g, $2J$, and $N\alpha$ were assumed to be 2.15, 62.8 cm^{-1}, and 60×10^{-6} emu/mol, respectively.

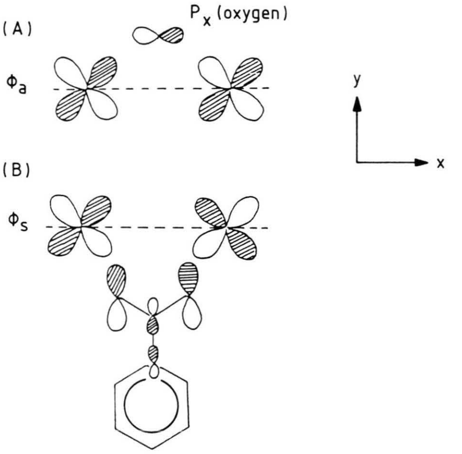


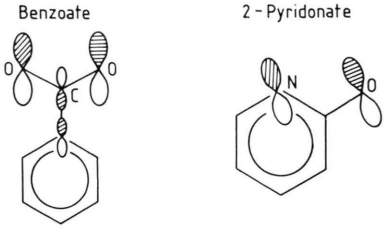
Fig. 3. Symmetric (φ_s) and antisymmetric (φ_a) combinations of metal d orbitals, and their interaction with ligand orbitals.

being defined as positive. The J_{AF} value can be written as [13]

$$J_{AF} = (\varepsilon_a - \varepsilon_s)^2/(J_{11} - J_{12})$$

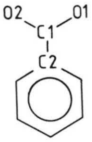
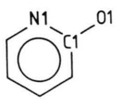
where ε_a and ε_s denote the energies of φ_a and φ_s orbitals in equations (1) and (2). Thus, we can anticipate that the larger the energy separation between φ_a and φ_s orbitals, the stronger is the antiferromagnetic interaction, irrespective of which combination of the orbitals (φ_a or φ_s) is lower in energy. On this basis, spin exchange interaction of hydroxo- or alkoxo-bridged copper(II) complexes can be reasonably explained in the following manner [4]. In such a system, the oxygen p_x orbital (bridging atom) interacts with a φ_a orbital to raise its energy, whereas is orthogonal to the φ_s orbital and exerts no effect on it (*cf.* Fig. 3). On the other hand, the effect of the p_y orbital on the φ_a and φ_s orbitals are reversed, *i. e.*, raising φ_s but not φ_a. If the Cu–O–Cu angle is larger than 90°, the effect of p_x on the orbitals exceeds that of p_y so that the larger energy separation of φ_a and φ_s orbitals brings about a stronger antiferromagnetism (in equation (3) J_{AF} is larger than J_F).

In the present case, the ligand orbitals of alkoxide and 2-pyridonate should be considered. Thus, we have calculated the energy levels of benzoate and 2-pyridonate in terms of CNDO/2 and MINDO/2 methods [14, 15], the results being briefly summarized in Table IV. The highest σ-donor orbitals of benzoate and 2-pyridonate are illustrated below:



In the case of the benzoate complex, the energy of the φ_s orbital is lifted through the interaction with this σ-donor orbital, but that of φ_a is left unaltered, as shown in Fig. 3. Therefore, when the copper(II) ions are linked by alkoxide and benzoate ions and the angle Cu–O–Cu (O: alkoxo oxygen) is larger than 90°, the energies of φ_s and φ_a orbitals are lifted by the benzoate and alkoxide bridges, respectively, resulting in a diminished energy separation of φ_s and φ_a orbitals as compared with that of a single-alkoxide bridged complex. Thus, the reduced $-2J$ value ($+190\ cm^{-1}$) is reasonably explained [6]. Since the orbital phase of the highest σ-donor orbital of 2-pyridonate is the same as that benzoate, we can anticipate weak antiferromagnetism for $[Cu_2(L)(2\text{-pyrido-}$

Table IV. CNDO/2 and MINDO/2 calculations on benzoate and 2-pyridonate anion.

	Benzoate	2-Pyridonate
		
CNDO/2	$E(\varphi_1) = -4.50$ eV $-0.600\ [p_y(O1)] - 0.600\ [p_y(O2)]$ $+0.230\ [p_y(C1)] - 0.359\ [p_y(C2)]$ +other small terms $E(\varphi_2) = -4.81$ eV $-0.353\ [p_y(O1)] + 0.585\ [p_x(O1)]$ $+0.353\ [p_y(O2)] + 0.585\ [p_x(O2)]$ $-0.224\ [p_x(C1)]$ + other small terms	$E(\varphi_1) = -3.80$ eV $-0.585\ [p_y(O1)] + 0.294\ [p_x(O1)]$ $-0.435\ [p_y(N1)] + 0.250\ [p_x(N1)]$ $+0.246\ [p_y(C1)] - 0.126\ [p_x(C1)]$ +other small terms
MINDO/2	$E(\varphi_1) = -4.19$ eV $+0.560\ [p_y(O1)] + 0.560\ [p_y(O2)]$ $-0.212\ [p_y(C1)] + 0.436\ [p_y(C2)]$ +other small terms $E(\varphi_2) = -4.27$ eV $-0.603\ [p_x(O1)] + 0.325\ [p_y(O1)]$ $-0.603\ [p_x(O2)] - 0.325\ [p_y(O2)]$ $+0.159\ [p_x(C1)]$ + other small terms	$E(\varphi_1) = -3.18$ eV $-0.378\ [p_y(O1)] + 0.141\ [p_x(O1)]$ $-0.648\ [p_y(N1)] + 0.213\ [p_x(N1)]$ $+0.216\ [p_y(C1)] - 0.118\ [p_x(C1)]$ +other small terms

nate)], but this is inconsistent with the experimental result.

According to Kahn *et al.* [16], J_{AF} is also dependent on the dihedral angle between the two planes containing the copper(II) ion, and reaches nearly zero when the dihedral angle decreases from 180 to 130°. In the present complex [Cu_2(L)(2-pyridonate)], the dihedral angle is 121°, which is near 130°. Thus, we can conclude that the ferromagnetism observed for [Cu_2(L)(2-pyridonate)] is mainly attributed to the small dihedral angle (negligible contributions of J_{AF}). Very recently Nishida *et al.* [17] have observed that weak antiferromagnetism is operating in a binuclear copper(II) complex with the dihedral angle of 90°, which is consistent with the calculated result by Kahn *et al.* [16]. These facts support the validity of the simple treatment by Hoffmann and Kahn *et al.* based on the "extended Hückel MO" when elucidating the superexchange interaction of binuclear copper(II) complexes.

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